OL Organic Letters

pubs.acs.org/OrgLett

Letter

Transition-Metal-Free, Formal C−H Germylation of Arenes and Styrenes via Dibenzothiophenium Salts

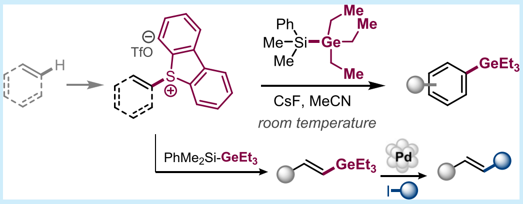
Aymane Selmani and Franziska Schoenebeck*

Cite This: *Org. Lett.* 2021, 23, 4779−4784

Read Online

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: We report an operationally simple, selective, and transition-metal-free germylation of arenes and styrenes at room temperature, using a robust and bench-stable Ge source (R_3Ge-SiR_3) and dibenzothiophenium salts as enabling intermediates. The first direct engagement in cross-coupling of the newly made *E*-alkenyl germanes is also presented, allowing the chemoselective arylation under air-tolerant nanoparticle catalysis.



Owing to their relatively high robustness, hydrophobicity, and low toxicity, organogermanes have found applications in drug discovery[1] and material science.[2] More recently, the potential of aryl germanes as alternative and orthogonal coupling partners in synthesis and catalysis has also been showcased,[3,4] which allows their selective functionalization in the presence of C-halogen, C-BPin, or C-silanes and therefore adds a dimension of versatility in the modular assembly of densely functionalized polyarenes. While alkylations of closely related germatranes could also recently be achieved,[5] the direct functionalization of alkenyl germanes remains unprecedented. In this context, the broader impact of organogermanes is directly correlated to their synthesizability, and as such, there is a significant demand for an efficient, selective, and practical methodology to install the Ge functionality into organic molecules. Ideally, this methodology is amenable to advanced building blocks to meet the need for late-stage diversification in a medicinal and material context on one hand and to be able to access diverse building blocks for modular synthesis on the other hand.[3] Classical syntheses of C_{sp2}-germanes rely on C_{sp2}-halides via stoichiometric organometallic reactivity[3,6] or transition metal catalysis,[7] albeit of limited scope owing to the basicity of reagents and/or the need for harsh reaction conditions. Moreover, the C-halogen sites would be of utmost value for modular building blocks (see Figure 1), and a synthetic strategy to introduce the Ge functionality in the presence of C-halogen would therefore be highly enabling. While direct C−H functionalization would be desired, such protocols suffer from the need of a directing group and high temperature (>90 °C), resulting in only a handful of *ortho*-germylated examples, and the employed transition metal is

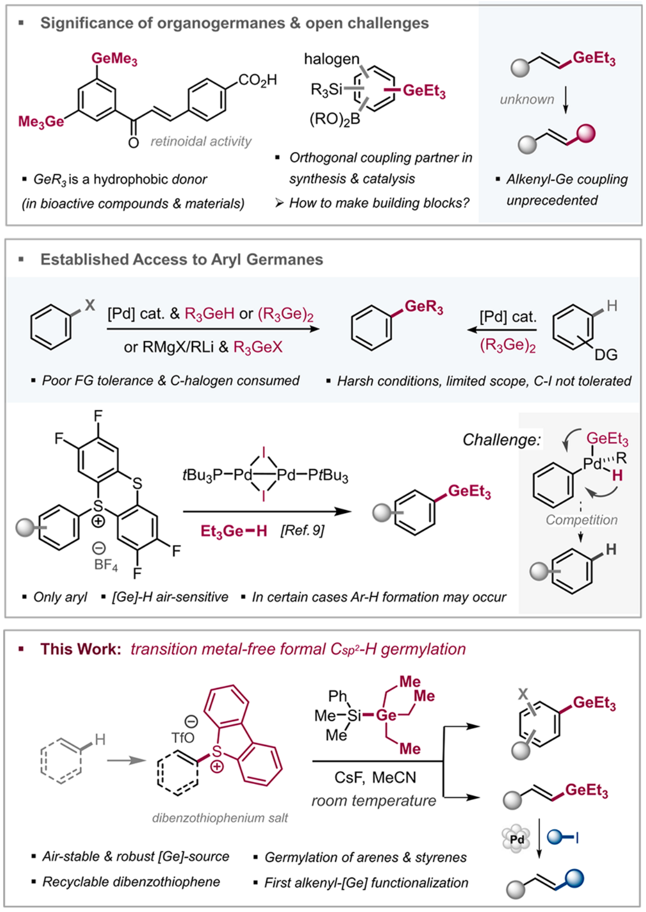


Figure 1. Significance and state-of-the-art of the aryl germane synthesis (top) and this work (bottom).

Received: May 2, 2021
Published: June 4, 2021

https://doi.org/10.1021/acs.orglett.1c01505
Org. Lett. 2021, 23, 4779−4784

incompatible with, e.g., C−I bonds.[8] By contrast, a mild and directing-group-free C−H germylation would greatly improve the diversity of accessible C_{sp2}-germanes. In this context, we recently reported a $Pd^{(I)}$-dimer-catalyzed[9] germylation via formal C−H functionalization of nonactivated and directing-group-free arenes, enabled by (tetrafluoro)thianthrenium salts as key intermediates and using triethylgermane (Et_3GeH) as a reagent (Figure 1).[10] While the method was mild, it was limited to arenes, and a competitive side reaction with the air-sensitive Et_3GeH was encountered in some cases, which generates Ar−H as the byproduct.[7a,b,11]

With a view to develop a more efficient, practical, and selective method that expands the accessible substrates also to olefins, we set out to develop a transition-metal-free germylation of C_{sp2}-sites using a robust and air-stable Ge reagent. Moreover, we showcase the first direct coupling of alkenyl germanes.

To this end, we further focused on C_{sp2}-SR_2 salts, which were shown to be powerful linchpins. Recently, Lewis,[12] Procter,[13] and Ritter[14] demonstrated that aryl and alkenyl sulfonium salts (such as (tetrafluoro)thianthrenium and dibenzothiophenium) were readily introduced by formal C−H functionalization of arenes or olefins in a site-selective manner, providing a versatile platform for functionalizations in C−C, C−N, C−O, C−Hal, SiR_3, or BR_2 bond formations with transition metal and/or photoredox catalysis.[12−17] Under metal-free conditions,[18] the borylation of thiol-derived sulfonium salts, i.e., $ArSMe_2^+$, under UV light with limited functional group tolerance has been reported,[19] and for highly activated $ArSMe_2^+$ salts that bear an electron-withdrawing substituent in the para-position, silylation and stannylation using R_3Si-SiR_3 or R_3Sn-SnR_3 under CsF activation could recently be achieved without an added transition metal.[20a] However, our attempts to extend this methodology to the corresponding germylation of $PhSMe_2^+$ (or alkenyl-SMe_2^+) failed to produce the corresponding organogermanes.[20b]

With the aim to identify a suitable nucleophilic [Ge] source and move away from the unstable [Ge]−H reagent, we envisioned that a [Ge−Si] reagent might allow us to liberate a $[R_3Ge]^-$ nucleophile *in situ* and as such circumvent the need for any transition metal catalyst. We focused on $PhMe_2Si$-$GeEt_3$,[21,22] which presents high air and moisture stability paired with storability at room temperature[23] and has been shown to liberate the desired [Ge] anion over the [Si] anion under TBAF activation, which allowed us to substitute aryl bromides to the corresponding aryl germanes, albeit under moderate yield (approximately 35−40%) and under Ar−H byproduct formation.[24] Indeed, our computational studies at the CPCM (MeCN) M06-2X/6-311++G(d,p) level of theory confirmed that attack of a fluoride anion at Si over the alternative attack at Ge is both kinetically (by $\Delta\Delta G^\ddagger$ = 10.1 kcal/mol) and thermodynamically (by $\Delta\Delta G_{rxn}$ = 15.2 kcal/mol) favored (see SI for a complete profile).[25]

The reagent $PhMe_2Si$-$GeEt_3$ can be readily prepared from the chlorosilane $PhMe_2SiCl$, in the presence of lithium naphthalenide, and Et_3GeCl in high yield (4.48 g, 76% yield).[21] In this manner, analogous [Ge−Si] compounds are also accessible by varying the employed chlorogermane R_3GeCl. For example, we synthesized $PhMe_2Si$-Ge^nBu_3 in 63% yield.

However, when we subjected $PhMe_2Si$-$GeEt_3$ along with CsF to a (tetrafluoro)thianthrenium salt, which we previously germylated under $Pd^{(I)}$ dimer catalysis,[10] the corresponding aryl germane did not result in the absence of a transition metal (see Figure 2). Instead, one of the C−S bonds of the thianthrene moiety was cleaved instead of *ipso*-substitution.[26]

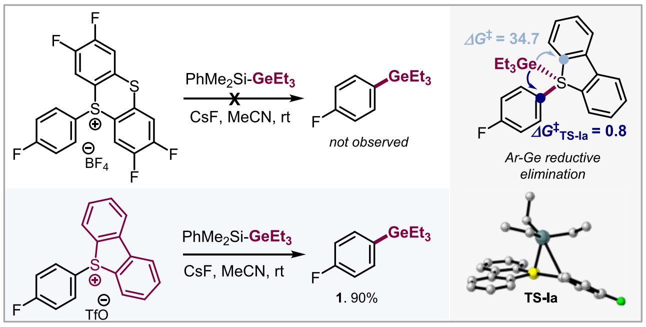


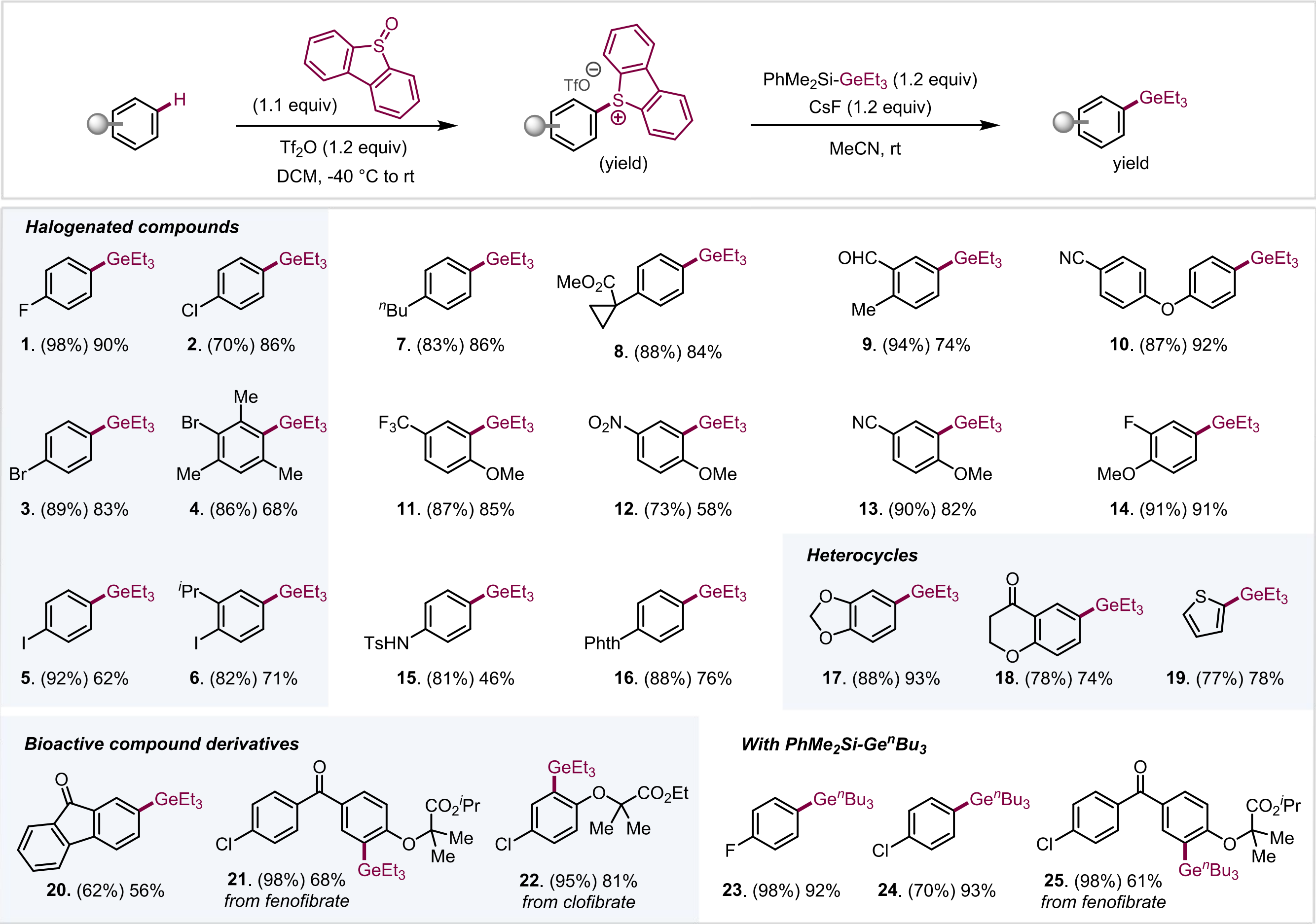
Figure 2. Rationalization of the regioselectivity in the germylation of 4-fluorophenyl dibenzothiophenium salt. Free energy differences are given in kcal/mol.

We therefore embarked on investigating alternative sulfonium salts that can readily be made from arenes directly via C−H functionalization. In this context, dibenzothiophenium salts have previously been shown to give high reactivity toward direct *ipso*-substitution in aromatic $[^{18}F]$-fluorination.[14e,18b] Our computational studies[25] of this salt indicated that the Et_3Ge^- anion would initially add to the sulfur to adopt a trigonal bipyramidal sulfurane adduct,[27] which subsequently undergoes ligand coupling[13b] with an activation free energy barrier of $\Delta G^\ddagger$ = 0.8 kcal/mol to yield the desired $ArGeEt_3$ (see Figure 2 and SI for a complete profile). This process is $\Delta\Delta G^\ddagger$ = 33.9 kcal/mol favored over the alternative bond cleavage to break the dibenzothiophene bond. These observations parallel previous computational studies of the functionalization of sulfonium salts.[18b] Encouraged by these data, we set out to experimentally explore this transformation.

Upon testing a range of fluoride sources and solvents, to our delight, we identified that germylation of 4-fluorophenyl dibenzothiophenium salt with $PhMe_2Si$-$GeEt_3$ proceeded very efficiently at room temperature in MeCN with CsF, giving the desired 4-fluorophenyl triethylgermane in 90% yield (Figure 2). No side products arising from silylation were detected; $PhMe_2Si$-F was observed by GC-MS analysis, whereas Et_3Ge-F was not detected, showcasing the high chemoselectivity in the activation of the [Ge−Si] reagent. Notably, our tests with the alternative digermane Et_6Ge_2 reagent in place of $PhMe_2Si$-$GeEt_3$ under otherwise identical conditions did not give rise to conversion, indicating that Et_6Ge_2 cannot be activated in this manner with a fluoride source. We also tested alternative electrophiles for the germylation; however, no germylation occurred with the corresponding aryl iodide, bromide, triflate, dimethylsulfonium, or tetrafluorothianthrenium salts, and only the dibenzothiophenium salt gave rise to the aryl germane.

With the reaction conditions in hand, we next examined the scope of this two-step germylation process. The protocol proved to be effective for a range of compounds; there was no marked influence of steric or electronic effects on the reaction efficiency. Access to halogenated aryl germanes was possible, leading to valuable scaffolds for further diversification opportunities (**1**−**6**). Electron-rich (**7**) and -poor arenes (**8**−**9**) reacted well, in both dibenzothiophenylation and germylation reactions, to afford the corresponding aryl

Scheme 1. Substrate Scope of the Transition-Metal-Free and Site-Selective Germylation of Arenes[a]



[a] Reaction conditions for the first step: arene (1.0 equiv), dibenzothiophene-*S*-oxide (1.1 equiv), Tf_2O (1.2 equiv) in DCM (0.25 M), −40 °C to rt. Yields are given for isolated products in parentheses. Reaction conditions for the second step: aryl dibenzothiophenium salt (1.0 equiv), $PhMe_2Si$-$GeEt_3$ (1.2 equiv), and CsF (1.2 equiv) in MeCN (0.1 M), rt. Yields are given for isolated products.

triethylgermanes in high yields. Several anisole derivatives, with trifluoromethyl (**11**), nitro (**12**), nitrile (**13**), or fluorine (**14**) as substituents in various positions, were successfully converted, showcasing the excellent site selectivity, as no other regioisomers were observed. Aniline-containing triethylgermanes could also be synthesized (**15**−**16**). The process is also compatible with heterocycles (**17**−**19**).

Within the realm of late-stage functionalization, we also investigated the possibility for germylation of drug-like molecules and bioactive compounds. The formal C−H germylation of fenofibrate (**21**) and clofibrate (**22**) was selectively achieved in good yields. It is important to note that reduction of the aryl dibenzothiophenium salt to Ar−H was fully prevented using the $PhMe_2Si$-$GeEt_3$ reagent, which contrasts the previous metal-catalyzed development with Et_3GeH.[10] Moreover, the introduction of alternative R_3Ge groups is also possible through modification of the R_3Ge-$SiMe_2Ph$ reagent.[28] To illustrate this, we synthesized tri-*n*-butylgermanes (**23**−**25**) in this manner (Scheme 1).

With the efficient formal C−H germylation of arenes demonstrated, we subsequently set out to investigate the C−H germylation of alkenes. Alkenyl germanes are currently accessible from the corresponding vinyl halides (via metalation and quenching with Ge-electrophile)[29] or the hydrogermylation of alkynes.[30]

However, to date, there has not been a precedence of direct C−C coupling of alkenyl germanes. In fact, in attempts to couple alkenyl germanes under Pd catalysis, their halogenation was instead conducted (under harsh conditions using I−Cl, neat at 85 °C).[30d]

We therefore next set out to investigate the germylation of the corresponding alkenyl dibenzothiophenium salts. While the synthesis and C_{sp2}−C_{sp2} coupling of styryl sulfonium salts have previously been established,[13b,c] their germylation (as well as conceptually similar silylation or borylation) has not been demonstrated. To our delight, we observed smooth germylation of styrenes (after initial C−H dibenzothiophenylation), using the same conditions as for the arenes. We successfully prepared a variety of diversely substituted styrenes in high yield, including examples that contained sensitive C-halogen sites (**27**−**28**). Notably, the (*E*)-isomer was exclusively formed in all cases (Figure 3, top). With these styryl triethylgermanes in hand, we subsequently explored their reactivity with the aim to establish their first direct engagement in C−C cross-coupling reactivity with aryl halides.

Building on our previous findings of orthogonal nanoparticle catalysis with aryl germanes,[3f] we found that the employment of Pd-nanoparticle conditions allowed the direct cross-coupling of aryl iodides with our newly synthesized alkenyl germanes. Notably, the coupling was fully *E*-selective and privileged at the

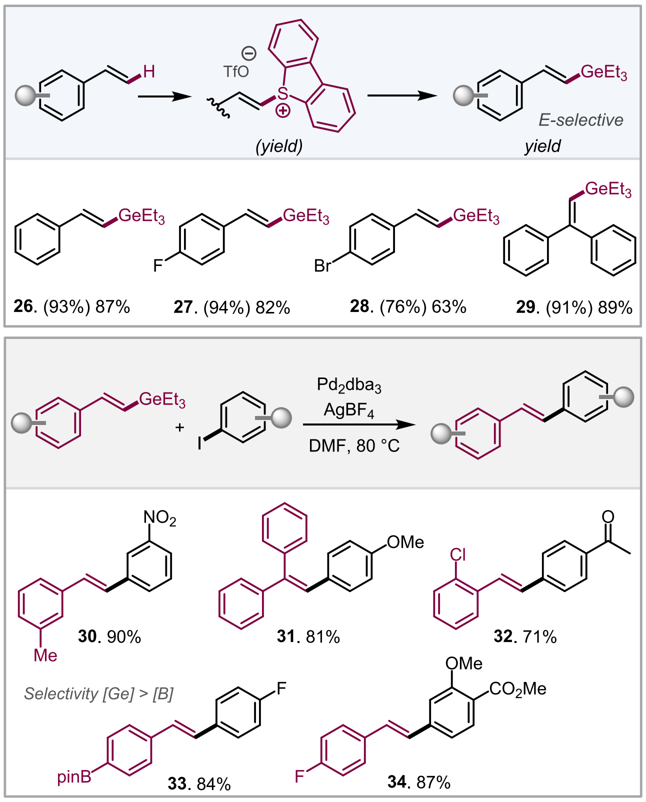


Figure 3. Synthesis of styryl germanes from styrenes (top) and Pd-catalyzed cross-coupling of styryl germanes with aryl iodides (bottom). (See SI for reaction conditions).

Ge site, leaving the competing C−BPin or C−Cl sites completely untouched (Figure 3, bottom). This constitutes the first example of direct cross-coupling of alkenyl trialkylgermane and emphasizes their wider potential in chemoselective cross-couplings for the rapid and modular buildup of molecules.

For operational simplicity of the protocol, we also tested the possibility of a telescoped reaction sequence starting from the arene or styrene directly,[31] which would avoid the separate isolation and purification of the dibenzothiophenium salt intermediates. We found that a simple solvent switch after the initial C−H dibenzothiophenylation from DCM to MeCN was sufficient to ultimately obtain aryl or alkenyl germanes,[13c] albeit in moderate yield. An added filtration of the dibenzothiophenylation reaction mixture (over a pad of $NaHCO_3$ and $MgSO_4$) along with the solvent switch increased the yields of the germylated products drastically (Figure 4). Importantly, this telescoping approach was found to be applicable to the synthesis of both styryl as well as aryl germanes.

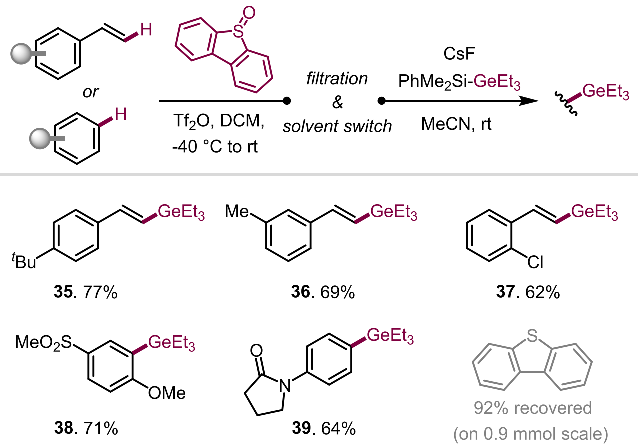


Figure 4. Straightforward germylation of arenes and styrenes via a telescoped reaction without isolation of intermediate salts and recovery of dibenzothiophene.

As the dibenzothiophene is regenerated in the transformation, it can readily be recovered by column chromatography in pentane. For the synthesis of **39** (187 mg, 65% yield) from 1-phenyl-2-pyrrolidinone (0.09 mmol scale), we were able to recover dibenzothiophene (168 mg) in 92% yield.

In conclusion, we developed an operationally simple, selective, and transition-metal-free germylation of arenes and styrenes at room temperature via formal C−H functionalization, enabled by dibenzothiophenium salts as key intermediates. The protocol makes use of a robust, bench-stable, and readily accessible $R_3Ge\text{-}SiR_3$ reagent and is applicable to various arenes and styrenes, delivering the corresponding *E*-alkenes exclusively. Moreover, the first direct arylation of the alkenyl germanes was also showcased, which proceeds efficiently under Pd-nanoparticle catalysis with aryl iodides (also in air) in a fully orthogonal manner to established coupling regimes, as competing C-BPin or C-halogen sites are tolerated in the coupling process. Owing to the potential of C_{sp2}-germanes as functional molecules as well as orthogonal coupling partners in synthesis and catalysis paired with the simplicity of the presented method (mild conditions, recoverable dibenzothiophene, and bench-stable reagents), we anticipate widespread interest in the described methodology in academia and industry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01505.

Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra of the new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Franziska Schoenebeck − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany;* orcid.org/0000-0003-0047-0929;
Email: franziska.schoenebeck@rwth-aachen.de

Author

Aymane Selmani − *Institute of Organic Chemistry, RWTH Aachen University, 52074 Aachen, Germany*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.orglett.1c01505

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Calculations were performed with computing resources granted by JARA-HPC from RWTH Aachen University under project "jara0091".

■ REFERENCES

(1) For examples, see: (a) Fujii, S.; Miyajima, Y.; Masuno, H.; Kagechika, H. *J. Med. Chem.* **2013**, *56*, 160−166. (b) Yamakawa, T.; Kagechika, H.; Kawachi, E.; Hashimoto, Y.; Shudo, K. *J. Med. Chem.* **1990**, *33*, 1430−1437.

(2) For examples, see: (a) Zaitsev, K. V.; Lam, K.; Poleshchuk, O. K.; Kuz'mina, L. G.; Churakov, A. V. *Dalton Trans* **2018**, *47*, 5431−5444. (b) Su, T. A.; Li, H.; Klausen, R. S.; Kim, N. T.; Neupane, M.; Leighton, J. L.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. *Acc. Chem. Res.* **2017**, *50*, 1088−1095. (c) Kachian, J. S.; Wong, K. T.; Bent, S. F. *Acc. Chem. Res.* **2010**, *43*, 346−355. (d) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271−1308.

(3) (a) Fricke, C.; Schoenebeck, F. *Acc. Chem. Res.* **2020**, *53*, 2715−2725. (b) Fricke, C.; Deckers, K.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2020**, *59*, 18717−18722. (c) Sherborne, G. J.; Gevondian, A. G.; Funes-Ardoiz, I.; Dahiya, A.; Fricke, C.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2020**, *59*, 15543−15548. (d) Dahiya, A.; Fricke, C.; Schoenebeck, F. *J. Am. Chem. Soc.* **2020**, *142*, 7754−7759. (e) Fricke, C.; Dahiya, A.; Reid, W. B.; Schoenebeck, F. *ACS Catal.* **2019**, *9*, 9231−9236. (f) Fricke, C.; Sherborne, G. J.; Funes-Ardoiz, I.; Senol, E.; Guven, S.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2019**, *58*, 17788−17795.

(4) For other uses in cross-coupling, see: (a) Xu, M. Y.; Jiang, W. T.; Li, Y.; Xu, Q. H.; Zhou, Q. L.; Yang, S.; Xiao, B. *J. Am. Chem. Soc.* **2019**, *141*, 7582−7588. (b) Song, H. J.; Jiang, W. T.; Zhou, Q. L.; Xu, M. Y.; Xiao, B. *ACS Catal.* **2018**, *8*, 9287−9291. (c) Zhang, Z. T.; Pitteloud, J. P.; Cabrera, L.; Liang, Y.; Toribio, M.; Wnuk, S. F. *Org. Lett.* **2010**, *12*, 816−819. (d) Pitteloud, J. P.; Zhang, Z. T.; Liang, Y.; Cabrera, L.; Wnuk, S. F. *J. Org. Chem.* **2010**, *75*, 8199−8212.

(5) (a) Jiang, W. T.; Xu, M. Y.; Yang, S.; Xie, X. Y.; Xiao, B. *Angew. Chem., Int. Ed.* **2020**, *59*, 20450−20454. (b) Xu, M. Y.; Jiang, W. T.; Li, Y.; Xu, Q. H.; Zhou, Q. L.; Yang, S.; Xiao, B. *J. Am. Chem. Soc.* **2019**, *141*, 7582−7588.

(6) Langle, S.; David-Quillot, F.; Balland, A.; Abarbri, M.; Duchêne, A. *J. Organomet. Chem.* **2003**, *671*, 113−119.

(7) (a) Komami, N.; Matsuoka, K.; Yoshino, T.; Matsunaga, S. *Synthesis* **2018**, *50*, 2067−2075. (b) Lesbani, A.; Kondo, H.; Yabusaki, Y.; Nakai, M.; Yamanoi, Y.; Nishihara, H. *Chem. - Eur. J.* **2010**, *16*, 13519−13527. (c) Nakamura, T.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2002**, *4*, 3165−3167. (d) Azarian, D.; Dua, S. S.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C55−C57.

(8) (a) Elsby, M. R.; Liu, J.; Zhu, S.; Hu, L.; Huang, G.; Johnson, S. A. *Organometallics* **2019**, *38*, 436−450. (b) Chen, C.; Guan, M.; Zhang, J.; Wen, Z.; Zhao, Y. *Org. Lett.* **2015**, *17*, 3646−3649. (c) Kanyiva, K. S.; Kuninobu, Y.; Kanai, M. *Org. Lett.* **2014**, *16*, 1968−1971. For an example of *meta*-selective C−H germylation, see: (d) Modak, A.; Patra, T.; Chowdhury, R.; Raul, S.; Maiti, D. *Organometallics* **2017**, *36*, 2418−2423.

(9) For selected applications on $Pd^{(I)}$ dimer catalysis, see: (a) Mendel, M.; Kalvet, I.; Hupperich, D.; Magnin, G.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2020**, *59*, 2115−2119. (b) Kalvet, I.; Deckers, K.; Funes-Ardoiz, I.; Magnin, G.; Sperger, T.; Kremer, M.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2020**, *59*, 7721−7725. (c) Magnin, G.; Clifton, J.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2019**, *58*, 10179−10183. (d) Chen, X. Y.; Pu, M.; Cheng, H. G.; Sperger, T.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2019**, *58*, 11395−11399. (e) Scattolin, T.; Senol, E.; Yin, G.; Guo, Q.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2018**, *57*, 12425−12429. (f) Keaveney, S. T.; Kundu, G.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2018**, *57*, 12573−12577. (g) Kalvet, I.; Magnin, G.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2017**, *56*, 1581−1585.

(10) Selmani, A.; Gevondian, A. G.; Schoenebeck, F. *Org. Lett.* **2020**, *22*, 4802−4805.

(11) For a mechanistic study on silylation, see: Xu, Z.; Xu, J. Z.; Zhang, J.; Zheng, Z. J.; Cao, J.; Cui, Y. M.; Xu, L. W. *Chem. - Asian J.* **2017**, *12*, 1749−1757.

(12) Cowper, P.; Jin, Y.; Turton, M. D.; Kociok-Kohn, G.; Lewis, S. E. *Angew. Chem., Int. Ed.* **2016**, *55*, 2564−2568.

(13) (a) Aukland, M. H.; Siauciulis, M.; West, A.; Perry, G. J. P.; Procter, D. J. *Nat. Catal.* **2020**, *3*, 163−169. (b) Siauciulis, M.; Ahlsten, N.; Pulis, A. P.; Procter, D. J. *Angew. Chem., Int. Ed.* **2019**, *58*, 8779−8783. (c) Aukland, M. H.; Talbot, F. J. T.; Fernandez-Salas, J. A.; Ball, M.; Pulis, A. P.; Procter, D. J. *Angew. Chem., Int. Ed.* **2018**, *57*, 9785−9789.

(14) (a) Li, J.; Chen, J.; Sang, R.; Ham, W. S.; Plutschack, M. B.; Berger, F.; Chabbra, S.; Schnegg, A.; Genicot, C.; Ritter, T. *Nat. Chem.* **2020**, *12*, 56−62. (b) Berger, F.; Plutschack, M. B.; Riegger, J.; Yu, W.; Speicher, S.; Ho, M.; Frank, N.; Ritter, T. *Nature* **2019**, *567*, 223−228. (c) Sang, R.; Korkis, S. E.; Su, W.; Ye, F.; Engl, P. S.; Berger, F.; Ritter, T. *Angew. Chem., Int. Ed.* **2019**, *58*, 16161−16166. (d) Chen, J.; Li, J.; Plutschack, M. B.; Berger, F.; Ritter, T. *Angew. Chem., Int. Ed.* **2020**, *59*, 5616−5620. (e) Xu, P.; Zhao, D.; Berger, F.; Hamad, A.; Rickmeier, J.; Petzold, R.; Kondratiuk, M.; Bohdan, K.; Ritter, T. *Angew. Chem., Int. Ed.* **2020**, *59*, 1956−1960.

(15) For selected examples, see: (a) Nie, X. X.; Huang, Y. H.; Wang, P. *Org. Lett.* **2020**, *22*, 7716−7720. (b) Tian, Z. Y.; Wang, S. M.; Jia, S. J.; Song, H. X.; Zhang, C. P. *Org. Lett.* **2017**, *19*, 5454−5457. (c) Vasu, D.; Yorimitsu, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 7162−7166. (d) Lin, H.; Dong, X.; Li, Y.; Shen, Q.; Lu, L. *Eur. J. Org. Chem.* **2012**, *2012*, 4675−4679. (e) Srogl, J.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1997**, *119*, 12376−12377.

(16) Wu, Y.; Huang, Y. H.; Chen, X. Y.; Wang, P. *Org. Lett.* **2020**, *22*, 6657−6661.

(17) Minami, H.; Otsuka, S.; Nogi, K.; Yorimitsu, H. *ACS Catal.* **2018**, *8*, 579−583.

(18) Metal- and light-free transformations of sulfonium salts, via direct *ipso*-substitution of the SR_2 moiety, were shown for fluorination. See: (a) ref 14e. (b) Gendron, T.; Sander, K.; Cybulska, K.; Benhamou, L.; Sin, P. K. B.; Khan, A.; Wood, M.; Porter, M. J.; Arstad, E. *J. Am. Chem. Soc.* **2018**, *140*, 11125−11132. (c) Mu, L.; Fischer, C. R.; Holland, J. P.; Becaud, J.; Schubiger, P. A.; Schibli, R.; Ametamey, S. M.; Graham, K.; Stellfeld, T.; Dinkelborg, L. M.; Lehmann, L. *Eur. J. Org. Chem.* **2012**, *2012*, 889−892. Two methods enabled C−O and C−N bond formations from triarylsulfonium salts at high temperature, requiring a large excess of $[Ar_3S][OTf]$. For more details, see: (d) Ming, X. X.; Tian, Z. Y.; Zhang, C. P. *Chem. - Asian J.* **2019**, *14*, 3370−3379. (e) Tian, Z. Y.; Ming, X. X.; Teng, H. B.; Hu, Y. T.; Zhang, C. P. *Chem. - Eur. J.* **2018**, *24*, 13744−13748.

(19) Huang, C.; Feng, J.; Ma, R.; Fang, S.; Lu, T.; Tang, W.; Du, D.; Gao, J. *Org. Lett.* **2019**, *21*, 9688−9692.

(20) (a) Zhao, J. N.; Kayumov, M.; Wang, D. Y.; Zhang, A. *Org. Lett.* **2019**, *21*, 7303−7306. (b) Our attempts to germylate $PhSMe_2^+$ using $Et_3Ge\text{-}GeEt_3$ with CsF resulted in demethylation to PhSMe. With $PhMe_2Si\text{-}GeEt_3$ and CsF, only traces of $ArGeR_3$ were formed.

(21) For a report on synthesis of this reagent, see: Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Kondo, M. *J. Organomet. Chem.* **1972**, *43*, 293−305.

(22) (a) Ono, K.; Ishizuka, H.; Nakano, T. *J. Organomet. Chem.* **1999**, *587*, 144−148. (b) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974−979.

(23) For alternative metalated Ge-nucleophiles (lithium, magnesium, or zinc), see: Xue, W.; Mao, W.; Zhang, L.; Oestreich, M. *Angew. Chem., Int. Ed.* **2019**, *58*, 6440−6443.

(24) (a) Mochida, K.; Suzuki, H.; Nanba, M.; Kugita, T.; Yokoyama, Y. *J. Organomet. Chem.* **1995**, *499*, 83−88. (b) Kabaki, M.; Inoue, S.; Nagata, Y.; Sato, Y. *Synth. Commun.* **1990**, *20*, 3245−3252.

(25) Frisch, M. J. et al. *Gaussian09*, revision E.01. (see Supporting Information for full reference) (b) Calculations were performed at the CPCM (MeCN) M06-2X/6-311++G(d,p) level of theory.

(26) The "wrong" C−S bond cleavage has been reported in such *ipso*-substitutions. Also, for different transformations, see: (a) ref 14e. (b) Ref 18d. (c) Ye, Y.; Zhu, J.; Huang, Y. *Org. Lett.* **2021**, *23*, 2386−2391.

(27) The $[Ar\text{-}DBT^+][Et_3Ge^-]$ adduct is formed from 4-fluorophenyl dibenzothiophenium cation $Ar\text{-}DBT^+$ via a nucleophilic attack of Et_3Ge^- to the sulfur atom. See the SI for a full reaction profile.

(28) Introduction of a silyl moiety is also possible with $(PhMe_2Si)_2$ or $PhMe_2Si$-BPin under the same reaction conditions. Installation of BPin is also tolerated in the presence of B_2pin_2 at 80 °C in MeCN.

(29) David-Quillot, F.; Lunot, S.; Marsacq, D.; Duchêne, A. *Tetrahedron Lett.* **2000**, *41*, 4905−4907.

(30) (a) Debrauwer, V.; Turlik, A.; Rummler, L.; Prescimone, A.; Blanchard, N.; Houk, K. N.; Bizet, V. *J. Am. Chem. Soc.* **2020**, *142*, 11153−11164. (b) Liang, H.; Ji, Y. X.; Wang, R. H.; Zhang, Z. H.; Zhang, B. *Org. Lett.* **2019**, *21*, 2750−2754. (c) de la Vega-Hernandez, K.; Romain, E.; Coffinet, A.; Bijouard, K.; Gontard, G.; Chemla, F.; Ferreira, F.; Jackowski, O.; Perez-Luna, A. *J. Am. Chem. Soc.* **2018**, *140*, 17632−17642. (d) Schweizer, S.; Tresse, C.; Bisseret, P.; Lalevee, J.; Evano, G.; Blanchard, N. *Org. Lett.* **2015**, *17*, 1794−1797. (e) Itazaki, M.; Kamitani, M.; Nakazawa, H. *Chem. Commun.* **2011**, *47*, 7854−7856. (f) Matsuda, T.; Kadowaki, S.; Yamaguchi, Y.; Murakami, M. *Org. Lett.* **2010**, *12*, 1056−1058.

(31) For a definition of "telescoped reaction", see: Hayashi, Y. *Chem. Sci.* **2016**, *7*, 866−880.

https://doi.org/10.1021/acs.orglett.1c01505
Org. Lett. 2021, 23, 4779−4784